

WORK PLAN

**PLUTONIUM SPECIATION, SOLUBILIZATION, AND MIGRATION
IN SOILS AND SEDIMENT AT THE ROCKY FLATS
ENVIRONMENTAL TECHNOLOGY SITE**

FEBRUARY 19, 1998

LOS ALAMOS NATIONAL LABORATORY

MAR 23 1998

ADMIN RECORD
A-SW-002651

Plutonium Speciation, Solubilization, and Migration in Soils and Sediment at the Rocky Flats Environmental Technology Site
Principal Investigators: Mary Neu, Wolfgang Runde (Los Alamos National Laboratory)

Science Area(s): Heavy Element Chemistry

EM-50 Need Area(s): Remedial Action

Award Year: 1997

Major Collaborator: Richard G. Haire (Oak Ridge National Laboratory)

Summary of Research: This project will study the chemical behavior of the toxic metal plutonium in contaminated soil on DOE sites in order to understand risks to the public and the environment and to develop appropriate cleanup methods.

Description of Research: The DOE is currently conducting cleanup activities at its nuclear weapons development sites, many of which have accumulated plutonium (Pu) in soils for 50 years. There is scientific uncertainty about the levels of risk to human health posed by this accumulation and whether Pu is migrating from Federal reserves onto public lands. To properly control Pu migration in soils, better evaluate the public risk, and design effective remediation strategies, a fundamental understanding of Pu speciation, transport, and release mechanisms is critically needed. Key elements of this proposal are:

- Determination of Pu oxidation state(s) and speciation in selected pond sediments and soil samples. Implementation and development of techniques that characterize chemical speciation of Pu in these soils will be applicable for other sites and will increase our understanding of actinide environmental chemistry. Particular focus is on particulate, colloid and dissolved relationships.
- The Pu concentrations in settling ponds show seasonal variation that correlate with Mn concentrations. Actual pond sediment samples will be used to evaluate the impact of mineral redox cycling on Pu solubility and mobility. Laboratory studies using synthetic Mn/Fe minerals and Pu species will be performed in parallel to determine the interaction mechanisms between Pu and these minerals and the potential for change in Pu mobility due to redox cycling.
- Thermal Ionization Mass Spectrometry (TIMS) analysis will be used to establish plutonium concentrations and distributions in soils at RFETS, to better understand Pu pathways from contamination sources and to enhance the assessment of public risk from actinide migration.
- Chemical systems important in Pu environmental behavior will be studied, providing critical thermodynamic data, as well as structural and chemical models for environmental samples. The Pu (III, IV, and V) species to be

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investigated may include: colloidal Pu(IV) hydroxide, $\text{Pu}(\text{OH})_x(\text{CO}_3)_y^{4-x-2y}$,
 PuO_2^+ , $\text{Pu}(\text{CO}_3)^+$, $\text{Pu}(\text{OH})_x^{3-x}$, and $\text{PuO}_2\text{CO}_3^-$.

- Results of studies will provide data for control and prediction of Pu release, metal chemistry in groundwaters and soils, thermodynamic modeling, site decontamination, and risk assessment.

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TIMETABLE OF PROPOSED WORK

FY 1998.

Proposed Accomplishments:

- Determine the isotopic distributions of Pu in soils and sediments at RFETS.
- Obtain and analyze samples from Pond C-2 and B-1.
- Identify the dominant species and redox state(s) of Pu and contaminated soils.

Approach

Our initial focus will be three-fold: 1) Define the Pu in soils at RFETS based on Rocky Flats and global fallout sources using isotopic ratios. 2) Obtain water and sediment samples from Ponds (C-2 and B-1) and begin characterization. 3) Obtain soil samples in which Pu is most highly concentrated in Pu and begin characterization.

We will determine the overall Pu content and isotopic ratios for sediments and waters from RFETS using TIMS. We will characterize the Pu in soil samples by determining morphology, degree of mineralization, and bulk distribution between types of phases using sequential filtration and a scanning electron microscope (SEM). We will measure the overall Pu oxidation state distribution using x-ray adsorption near edge spectroscopy (XANES) and attempt to identify the species by comparing the extended x-ray adsorption fine structure spectroscopy (EXAFS) with our growing database of actinide compounds. (XANES is used to investigate redox states of actinides; the adsorption edge position in the spectra is a function of electronic structure of the redox state. EXAFS is used to investigate the structure around the actinide atom, by evaluating the radial distribution of atoms; the spectra give peaks which are a function of distance from the atom of interest and number of atoms at that distance.)

Pond C-2 appears to undergo seasonal variations in Pu content associated with transition metal redox processes. Oxidation state distribution determined using XANES analysis will allow us to determine if solubility changes can be attributed to actinide redox changes. Sequential filtration studies may indicate the size distribution of host particle and allow us to determine if Pu is migrating via resuspended particles or via redox transformation to different chemical species.

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TIMETABLE OF PROPOSED WORK

FY 1999.

Proposed Accomplishments:

- Determine whether actinides are strongly bound to Mn oxide phases.
- Identify the metal/mineral interaction mechanism or mechanisms.
- Determine how those interactions change when the Mn is in oxidized and reduced states.
- Determine Mn mineral changes dictate changes in the oxidation state of Pu; *i.e.*, Is PuO_2^+ reduced to the much more strongly sorbed and less mobile Pu^{4+} ? Or is Pu^{4+} reduced to the also strongly sorbing Pu^{3+} ?

Approach

This FY we will continue to characterize the Pu in RFETS soils and we will perform laboratory studies on Pu carbonate and hydroxo species and Pu sorbed onto Mn oxide.

Soils characterization studies from the first year will define of the Pu(III, IV, and V) carbonate and Pu(III and IV) hydroxide systems as targets for fundamental studies. Initially, we expect to focus on the environmentally most relevant forms of Pu(IV), including $\text{Pu}(\text{OH})_x(\text{CO}_3)_y^{4-x-2y}$ and dilute colloidal Pu(IV) hydroxide. Obtaining characteristic spectra and determining the stability and properties of the species will not only provide data to compare with environmental samples, but also allow us to unravel the equilibrium constants of this most challenging and important plutonium system.

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TIMETABLE OF PROPOSED WORK

FY 2000.

Proposed Accomplishments:

- Determine the relative importance of Pu redox and (psuedo) colloid formation for the migration of the actinide at contaminated sites.
- Gain insights about the basic speciation of Pu in the environment and the dominant mechanisms which affect actinide mobility in the environment.
- Contribute to more complete and accurate predictions of the risks associated with environmental radionuclide migration and basic characterization necessary for enhanced remediation techniques.

Approach

It is expected that work will continue on the applications of the various state-of-the-art characterization and analytical methods for Pu colloid in soils. Also in this year, we will continue the Mn/Pu redox cycle and Pu sorption mechanistic studies. Redox experiments will be extended to include Fe redox coupled and competitive processes with Pu colloids.